

X-764-71-190

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N71-25748

# DEVELOPMENT OF AN AIR FLOW THERMAL BALANCE CALORIMETER

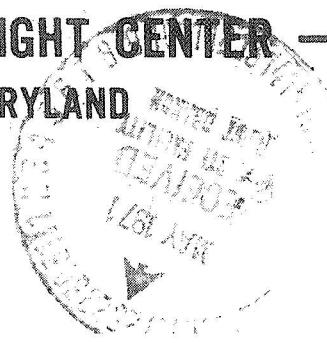
JOSEPH M. SHERFEY

MAY 1971

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— GODDARD SPACE FLIGHT CENTER —  
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THERMAL BALANCE CALORIMETER

Joseph M. Sherfey

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GODDARD SPACE FLIGHT CENTER  
Greenbelt, Maryland



## FOREWORD

The policy of NASA is to employ, in all formal publications, the international metric units known collectively as the *Système International d' Unites* and designated SI in all languages. In certain cases, however, utility requires that other systems of units be retained in addition to the SI units.

This document contains data so expressed because the use of the SI equivalents alone would impair communication. The non-SI units, followed in parentheses by their computed SI equivalents, are the basis of the measurements and calculations reported in this document.



DEVELOPMENT OF AN AIR FLOW  
THERMAL BALANCE CALORIMETER

Joseph M. Sherfey  
Engineering Physics Division

ABSTRACT

A new air flow calorimeter, based on the idea of balancing an unknown rate of heat evolution, with a known rate of heat evolution, is described. Under restricted conditions, the prototype system is capable of measuring thermal wattages from ten milliwatts to one watt, with an error no greater than one percent. Data are presented which reveal system weaknesses and point to modifications which would effect significant improvements.

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# DEVELOPMENT OF AN AIR FLOW THERMAL BALANCE CALORIMETER\*

by

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## I. INTRODUCTION

The United States space effort was little more than started when it became evident that there was a need for a calorimeter that could be used to measure the heat evolved by the electrochemical energy cells used as a source of electrical power on almost all spacecraft. Such measurements are needed to provide a suitable thermal balance on the spacecraft, and are especially important for space missions employing batteries of rechargeable nickel cadmium cells because such batteries are almost invariably the prime source of heat aboard a space vehicle.

This need for engineering data is paralleled by a need for scientific studies based on calorimetry. The processes attending the operation of most types of electrochemical cells are incompletely understood, and a well-planned program of studies based on calorimetric measurements would increase our knowledge in this important area.

In view of the many types of calorimeters that have been described in the scientific literature it would seem, a priori, that an existing calorimeter could be adapted to meet this need. This is actually not true because of a number of peculiar and rather stringent requirements which must be met by a calorimeter to be used for the type of measurements contemplated here. The following is a brief listing of these specialized needs.

### (1) Power vs. Energy

One important distinguishing characteristic derives from the fact that the quantity to be measured is not heat, as is the case with most calorimetric problems, but the time rate of heat evolution. In most instances the data needed can only be obtained while the cell under study is being subjected to repetitive cycles of charging and discharging, which simulate the anticipated space application. The purpose of such calorimetric measurements is to determine the rate at which the cell evolves heat as a function of time within this repetitive cycle. This information is needed to provide an adequate thermal balance on the spacecraft. The total heat evolved during a specific time interval can be computed, if needed, by arithmetic integration of these rate data with respect to time.

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\*Patent applied for.

## (2) Isothermal Operation

Performance that is characteristic of the cell is not observed until the cell has been exercised for a considerable length of time and has thus evolved a relatively large amount of heat. Because cell behavior is a sensitive function of cell temperature, this heat must be removed as fast as it is evolved in order to maintain the cell in an essentially isothermal condition. It follows that the calorimeter must be designed to meet this need.

## (3) Temperature Range

The previously mentioned sensitivity of the cell to temperature changes presents another constraint on calorimeter design – a need for the ability to operate the cell under study at any pre-determined constant temperature in the range from minus 10°C to plus 40°C (263K to 313K). Scientific studies would be benefited by an extension of this range in both directions.

## (4) Lead Problem

Probably the most difficult requirement to meet in designing an electrochemical calorimeter is a consequence of the relatively large electrical currents needed to operate the cell under study. Electrical devices in conventional calorimeters – heaters, for example – are designed to operate with large voltages and small currents. The purpose here is of course to minimize the diameter of the lead wires and thus the uncertainty due to heat transport leak along these wires. Electrochemical cells, quite unfortunately, are inherently low voltage, high current devices and therefore one cannot avoid the use of large leads. The severity of this problem is such that a calorimeter which is not designed to minimize the lead error can only be used for rough engineering measurements.

## (5) Endothermic Processes

The heat effect produced by the operation of an electrochemical cell can be divided into two parts, reversible and irreversible (Reference 1). Irreversible heat is a result of polarization at the electrodes and resistive effects in the terminals, electrodes, and electrolyte. This heat effect varies with the current in a complex and essentially unpredictable way but is always positive in the sense that it causes heat to be evolved.

The reversible part of the heat effect is a consequence of the entropy change ( $T\Delta S$ ) of the chemical reaction taking place in the cell, and on a molar or equivalent basis is independent of the rate of the reaction, i.e., the current. More importantly in the present context, it can cause heat to be either evolved or absorbed, depending on the direction of the cell reaction. For example, the entropy change which attends the charge reaction of the nickel cadmium cell causes heat to be absorbed. Therefore, in the case of this particular cell, if the reversible heat predominates over the irreversible heat the charge process will cause the temperature of this cell to decrease. Such cooling has been observed on numerous occasions.\*

It would be an exaggeration to say that an electrochemical calorimeter would be valueless if it were incapable of measuring endothermic processes. Many interesting and valuable experiments

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\*W. H. Metzger, Jr., M. Weinreb, and J. M. Sherfey, "Heat Effects of Nickel-Cadmium 'F' Cells," Goddard Space Flight Center, Document I-650-62-15, 1962.

are possible without encountering this phenomenon. This would be especially true for a cell such as the silver zinc cell with its relatively small entropy change. It is nonetheless true, however, that the ability to measure heat absorption is highly desirable and for most scientific programs it would be essential.

In spite of this rather formidable array of specialized requirements, quite a few workers have reported calorimetric studies of electrochemical cells. Most of these projects were based either on the use of an existing calorimeter design or on an instrument that was built hurriedly to meet an urgent and specific need. None of these calorimeters can be described as entirely satisfactory. Since most of these researches were not reported in the open literature, they are reviewed in the following section.

## II. LITERATURE SURVEY

The purpose of this section is to present a brief critical survey of the various calorimeters which have been used to measure the heat effects of electrochemical energy cells. Calorimetric studies that were directed at other areas of electrochemistry are not included. The same is true of researches concerning calorimeters that were not intended primarily for use with energy cells, even though such calorimeters might be adapted to this application.

The first series of measurements of the heat effects of energy cells was probably that initiated by Metzger, Weinreb, and Sherfey\* and extended by Metzger and Sherfey (Reference 2). This study was undertaken in order to solve an urgent thermal design problem on the first Nimbus spacecraft. The calorimeter used was a modified form of a calorimeter that had been developed for use in previous research (Reference 3). The cells under study were immersed in a light silicone oil which served as a calorimeter fluid and was contained by a glass dewar flask. The flask with its contents was completely immersed in a light hydrocarbon oil which acted as an adiabatic environment. The various calorimeter components such as the stirrer, platinum resistance thermometer, heater, adiabatic thermopile, and the leads to the cells, all passed through the adiabatic oil bath and then through appropriate seals in the flask lid. Error caused by joule heating of the leads was minimized by the use of relatively heavy (0.3 cm) copper leads and the heat leak error, including that along the leads, was essentially eliminated by rigorous adiabatic control.

Previous work with this calorimeter (Reference 3) had demonstrated its accuracy, but its usefulness for the study of energy cells is severely limited by the fact that the temperature of the cells under study and of the calorimeter fluid was constantly rising during the test. The data obtained were therefore characteristic of a range of temperatures instead of being characteristic of a particular temperature. Additionally, it was possible to operate the system for only a relatively short time if excessive cell temperatures were to be avoided.

The same type of calorimeter was used by L. Wilson and S. Voltz (Reference 4) in a later study. This system was less elaborate and more prone to error than that previously described and

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\*W. H. Metzger, Jr., M. Weinreb, and J. M. Sherfey, "Heat Effects of Nickel Cadmium 'F' Cells." Goddard Space Flight Center, Document I-650-62-15, 1962.

was of course subject to the same criticism with regard to non-isothermal operation. These comments are equally applicable to the work of Daley and Schmidt (Reference 5) who employed a modified oxygen bomb calorimeter to study an experimental ammonia battery. Isothermal operation is probably less important in such a study.

Several workers have employed what might be called the "calibrated heat leak" design. D. J. Doan (Reference 6) seems to have been the first to use this approach. He wrapped the cell under study with insulated heater wire and then immersed the assembly in low viscosity silicone oil which was contained by a copper box. The latter was surrounded on all six sides by a second copper box and separated from it by one inch (2.54 cm) of thermal insulation. The whole assembly was suspended in a thermostated refrigerator equipped with a circulating fan.

The rate of heat rejection of the system was measured using a thermopile which sensed the difference in temperature between the inner and outer boxes. The device was calibrated by using the heater as a known source. T. R. Beck and F. S. Kemp (Reference 7) used a basically similar system to estimate the heat effect of the Lunar Orbiter battery.

The accuracy of calorimeters of this general type is limited by two basic weaknesses. First, there seems to be no effective way to exclude lead errors and, second, there is no simple relationship between the rate of heat rejection by the cell and the temperature difference between the inner and outer boxes. This objection is valid even if one assumes that at any given moment the cell and the inner box are isothermal at one temperature and that the outer box is isothermal at another. The source of this error is the poor conductivity of the insulation and the relatively large heat capacity of the assembly consisting of the inner box, insulation, and outer box. A calorimeter of this type will afford accurate data under steady state conditions, but a changing thermal load will cause an error not only in measurements of the instantaneous rate of heat flow but also in calculated values for total heat obtained by integrating a series of such instantaneous values with respect to time.

Such calorimeters are inexpensive and entirely satisfactory if a high degree of accuracy is not essential. Such was the case in the references cited.

In a current project, W. V. Johnston (Reference 8) is developing a calorimeter which should also be classified as a calibrated heat leak calorimeter, but by employing a highly ingenious strategy he largely eliminates both objections regarding the two heat leak calorimeters previously referenced. In this design the cell is supported on a platform which is maintained at constant temperature by heat from two sources, the cell under study and an electrical heater. The platform is supported by a copper rod which is split longitudinally into two halves that are electrically insulated from one another. The lower end of this rod terminates in a heat sink held at constant temperature by immersion in boiling liquid nitrogen. Heat leakage from the system through any path other than the copper rod is minimized by means of vacuum jackets and adiabatic shielding. The rod serves three functions: as a mechanical support for the cell and its platform; as a known, constant thermal path between the cell and the heat sink; and as the electrical leads to the cell.

Platform temperature is sensed by a thermistor, which is one element of the automatic feedback loop that controls the heater in such a way as to maintain the temperature of the platform at a constant value. The rate at which heat is being evolved by the cell is obtained as the difference between the heater wattage and the wattage needed to maintain the platform isothermal in the absence of any heat evolution by the cell. A small excess in power over and above the latter wattage would be needed when the cell reaction is endothermic.

The accuracy of this system has not been evaluated but the basic approach seems to be sound. One weakness in this design is perhaps worth mentioning. The copper rod is constantly transporting a fixed large amount of heat. A small percentage error in the measurement of this heat, e.g., 0.1 percent, would introduce a relatively large error in the estimated heat output of the cell when the latter is a small fraction of the total heat needed to keep the platform isothermal. In other words, it is to be expected that the percentage error will increase as the absolute magnitude of the measured heat decreases. This would in most cases be a matter of no concern if the data were intended for use in engineering design. On the other hand, this system weakness could curtail the usefulness of the device in scientific studies.

J. J. Rowlette (Reference 9) has described an interesting engineering type calorimeter being used to measure the heat generation rate of the silver zinc battery which is the main source of power for the Surveyor spacecraft. The battery under study is immersed in a liquid such as Freon II which is maintained at its boiling point. The heat evolved by the battery causes the liquid to change into vapor which is then condensed, collected, and measured. The volume of condensate collected per unit time affords a measure of the rate of heat evolution. The container for the Freon which surrounds the battery is itself immersed in a second and large container which is also filled with the same liquid. A heater in this second container keeps the liquid there actively boiling and thus insures an adiabatic environment for the inner container.

A detailed description of the construction and performance of this calorimeter is not yet available, but it has been ascertained\* that in its present state of development it will measure a maximum of 300 watts and that the uncertainty is constant at approximately 5 percent of this figure.

Gillibrand and Wilde (Reference 10) devised an adiabatic calorimeter which they used to study the lead acid cell and the nickel cadmium cell. The basic calorimetric approach was to keep the cell and its surroundings at the same temperature, thus causing the cell to act as its own heat sink. Then, using the temperature rise of the cell, one can compute the heat evolved provided the heat capacity of the cell is also known. The latter was determined in a separate experiment. The apparatus consisted essentially of an insulated box with an external tube containing a blower and a heater. The blower constantly drew air from the box, passed it through the tube and then discharged it back into the box. Thermistors were used to sense the difference in temperature between the cell and the air in the box which surrounded it. This difference was kept at a minimum by means of a feedback circuit which controlled the heater.

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\*P. S. DuPont, private communication. Hughes Aircraft Co., Los Angeles, California.



Bruins, Caulder, and Salkind (Reference 11) and Caulder (Reference 12) used the same type calorimeter to study the same cell types – lead acid and nickel cadmium. Caulder suggested the use of a peltier cooler in addition to the heater in order to study both endothermic and exothermic reactions.

This type calorimeter is attractive from the standpoints of cost and simplicity but has little else to commend it. With no heat sink other than the cell itself, it is to be expected that rising cell temperatures would severely limit the types of measurements that are possible. The temperature is not uniform from point to point on the case of an electrochemical cell and, as a consequence, precise adiabatic control is impossible. None of the above authors discuss the lead error.

The two remaining calorimeters to be described are both flow calorimeters in the sense that the rate of heat evolution is measured in terms of the temperature rise of a stream of liquid.

One such device was designed and built by the present author and then delivered to American University where it was studied, modified, and used by a series of graduate students\* \*\* (Reference 13) over a period of years. Reduced to its essentials, the device consisted of a chamber which contained both the cell under study and an electrical heater. A thermopile with one set of junctions in the inlet of the chamber and the other set in its outlet served to measure the temperature rise of a liquid, either oil or water, as it flowed at a constant rate through the chamber. A calibration curve which related heater wattage to thermopile output was established and then used to estimate the rate of heat evolution by the cell.

Experience with the Air Flow Thermal Balance Calorimeter (AFTBC) described in this report indicates that the readout from a calorimeter of the American University (A.U.) type is influenced by the geometry and position of the heat source. Webster,\*\*\* page 45, states that the A.U. instrument was insensitive to the position of the heater but if the change of position he referred to was small and axial, a significant change in output was not to be expected. At no time was it established that a given rate of heat evolution by a cell caused the same signal as the same rate of heat evolution by a heater. The error from this source could have been evaluated by using the cell as its own calibration heater, i.e., by bringing the cell to a steady state overcharge condition so that the electrical power supplied to the cell equaled the rate of heat dissipation by the cell. An alternative procedure would involve wrapping the cell with the heater wire. Neither test was made.

A more basic weakness in the A.U. calorimeter derives from the relatively large wattage equivalent of its background temperature instability. The practical result of this weakness in the case of the A.U. instrument was an uncertainty in the order of one to ten milliwatts. The impact of this uncertainty on a ten-milliwatt signal is most unpleasant to contemplate. The nature of this uncertainty and its source are treated more fully in the "Conclusions" section of this report.

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\* S. M. Caulder, "The Design and Development of a Liquid Flow Calorimeter." M.S. Thesis, American University, Washington, D.C., 1964.

\*\* W. H. Webster, Jr., "Design and Development of a Continuous Flow Calorimeter and Measurements of the Thermal Characteristics of Nickel-Cadmium Batteries." M.S. Thesis, American University, Washington, D.C., 1967.

\*\*\* W. H. Webster, Jr., "Design and Development of a Continuous Flow Calorimeter and Measurements of the Thermal Characteristics of Nickel-Cadmium Batteries." M.S. Thesis, American University, Washington, D.C., 1967.

In summary, instruments of the A.U. type, if adequate precautions are observed, are probably satisfactory for measuring relatively large amounts of power, but without changing basic conditions such as flow rate or chamber cross section, the same device will not be suitable for measuring small amounts of power.

S. Gross (Reference 14) has described a flow calorimeter which was developed to make engineering type measurements on silver cadmium cells. The principal component of this calorimeter was a flat metal structure which acted as a base plate and heat sink for the cell under study. A metal tube imbedded in this structure carried a stream of water which served to remove the evolved heat and thus maintain the plate at a prescribed, fixed temperature. Thermistors immersed in the inlet and outlet ports were used to measure the temperature increase of the water. The system was calibrated by means of electrical heaters imbedded in dummy cells. Both the test cell and its metal base plate were encased in thermal insulation to minimize heat losses.

This instrument was not designed to be either highly accurate or ultra-sensitive. One source of error — heat loss through the insulation — was evaluated, but no estimate was made of the lead error which under some operating conditions is undoubtedly substantial. This is nonetheless an attractive design for engineering measurements, and if evaluated in terms of convenience and cost effectiveness, it is difficult to improve upon.

### III. APPARATUS

For convenience in describing the system, we will discuss it in four parts, all of which are shown, at least partially, in Figure 1. Adopting the order in which they will be described below, these are, first, the air supply system, parts of which can be seen in the upper right background. The second component is the calorimeter proper, which is the large box-like object in the right foreground. To the immediate left of the calorimeter is the rack containing the various components of the feedback control system and, finally, on the extreme left, the rack housing the data acquisition system. The exact meaning of these terms will become evident when these four subdivisions of the system are described. The basic idea or calorimetric approach is presented first.

#### 1. Basic Calorimetric Approach

The basic idea underlying the calorimeter can be explained by considering two identical chambers, the first containing the cell under study and the second an electrical heater. A stream of air is passed through the two chambers in series by way of a connecting tube. Each chamber is equipped with a thermopile which senses the temperature change of the air stream caused by its passage through that chamber.

This apparatus can be operated in either of two modes, depending upon whether the cell is evolving or absorbing heat. If heat is being evolved, the two thermopiles are connected opposed and the heater is operated in such a way as to maintain the net thermopile output (NTO) in a null condition. When such a balance exists, the rate of heat evolution of the cell can be measured as the electrical power (in watts) being supplied to the heater.

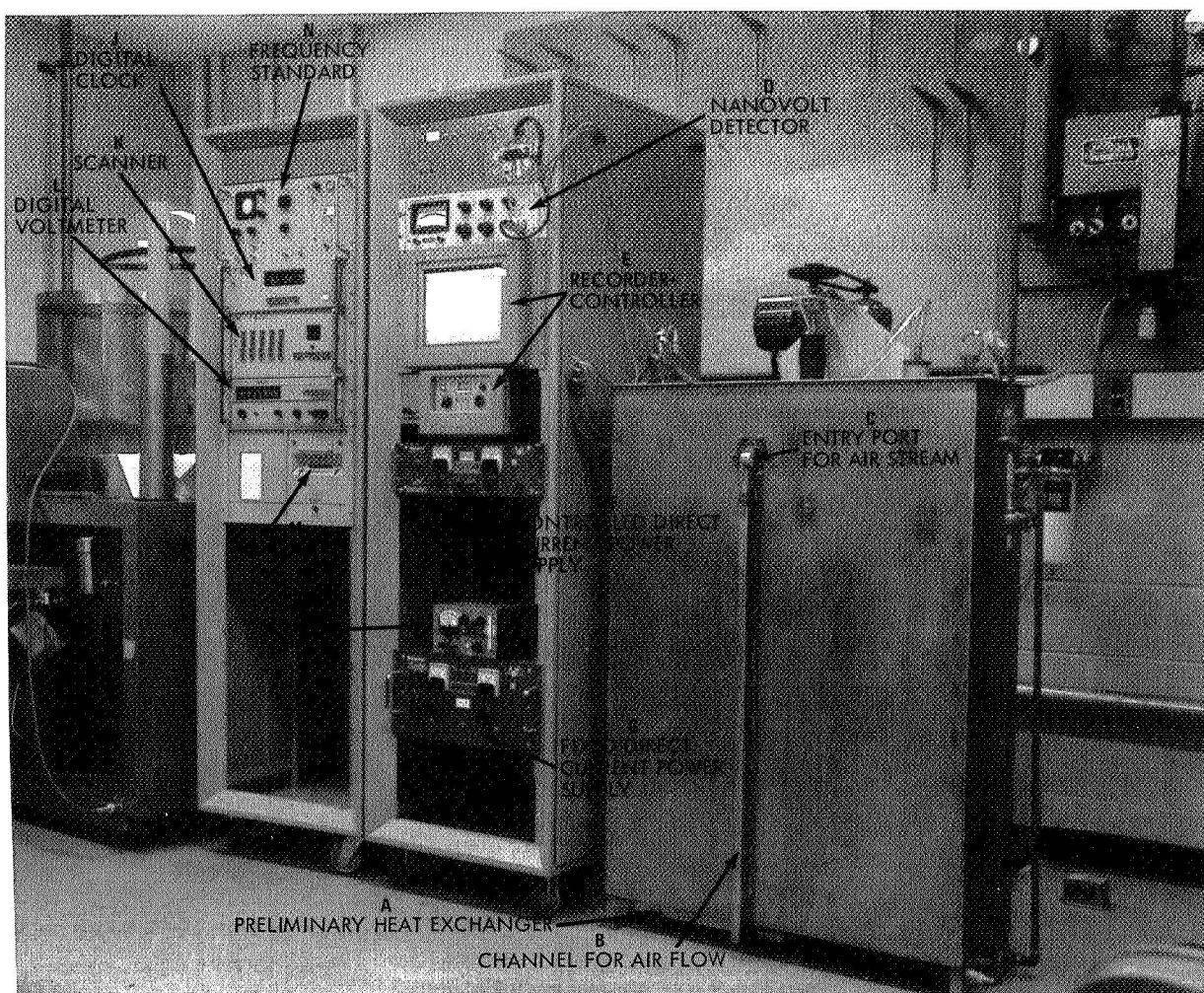


Figure 1. Photograph of Entire System. A-preliminary heat exchanger; B-channel for air flow; C-entry port for air stream; D-nanovolt detector; E-recorder-controller; F-controlled direct current powersupply; G-fixed direct current power supply; H-power supply; J-digital clock; K-scanner; L-digital voltmeter; M-printer; N-frequency standard.

If the cell is absorbing heat, only one chamber with its thermopile is needed and this chamber must be equipped with both a cell and a heater. When operating in this second mode, the idea is to balance the heat absorbed by the cell using the heat evolved by the heater. If these two heat effects are equal and opposite, the thermopile output will be zero and the cooling effect caused by the cell can be equated to the heater wattage.

Because the system has never been operated in this second mode, everything that follows applies exclusively to the first or exothermic mode of operation.

If the experimental objective is to measure the total heat evolved over a given time interval, the pertinent series of power measurements can be integrated with respect to time.

## 2. The Air Supply System

The air which flows through the calorimeter is drawn from a "house" supply which cycles in the pressure range 60 to 90 psig ( $4.13 \times 10^5$  to  $6.21 \times 10^5$  N/m<sup>2</sup>). This air passes first through a cutoff valve, then through a filter (a)\*, an automatic drying device (b), a second filter (c), a high pressure regulator (d), a low pressure regulator (e), a needle valve, a rotameter (f), a globe valve, and finally into the calorimeter. A short section of the air supply tube near the point where it connects to the calorimeter was removed and replaced with a length of rubber hose, to isolate the calorimeter electrically.

The high pressure regulator is adjusted to an output of about 40 psig ( $2.76 \times 10^5$  N/m<sup>2</sup>) and the low pressure regulator to about 20 psig ( $1.38 \times 10^5$  N/m<sup>2</sup>). This latter pressure is therefore applied to the input side of the needle valve. Air flow is adjusted and held constant by means of this valve which therefore acts as a throttling orifice.

The need for a gas dryer was discovered only after a long series of frustrating attempts to cure a violent and seemingly unexplainable instability in the output of the thermopiles while no heat was being supplied to either chamber. The source of this instability was eventually traced to fluctuations in the relative humidity of the air stream caused by cycling of the "house" air pressure between 60 and 90 psig ( $4.13 \times 10^5$  and  $6.21 \times 10^5$  N/m<sup>2</sup>). It is believed that the immediate cause of the temperature effects was a cyclic adsorption-desorption process on the inner walls of the heat exchangers (A and B, Figure 2) and, to a lesser extent, other parts of the calorimeter. There is no doubt about the need for controlling the humidity of the air stream.

## 3. The Calorimeter

A brief overview of the entire calorimeter will be presented first, using the diagrammatic representation in Figure 2 as a basis for the discussion. This overview will be followed by a detailed description of the various components.

Figure 2 shows that all the major calorimeter components are immersed in water which is contained by the jacket-vessel C and stirred by a propeller D. After entering the system, the air passes first through a heat exchanger A and then over a thermopile E which measures the temperature of the air relative to that of the water. The stream then passes down through the chimney F and into the calorimeter chamber G which contains the cell H under study and an electrical heater J. The lines at K represent the electrical leads needed to operate these two components. After the air exits from the calorimeter chamber, its temperature relative to that of the water is again measured by thermopile L. These components – heat exchanger, thermopiles, calorimeter chamber, etc. – are all duplicated on the other side of the system as represented in the diagram. The air stream finally passes out of the system through an exhaust tube M.

A. Jacket-Vessel and Heat Exchangers – Referring to Figure 2, C is a stainless steel jacket-vessel, 3 ft (91 cm) wide, 4 ft (122 cm) high, and 1 ft (30.5 cm) from front to back. Except for a

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\*The manufacturers of some equipment items are listed in the Appendix.

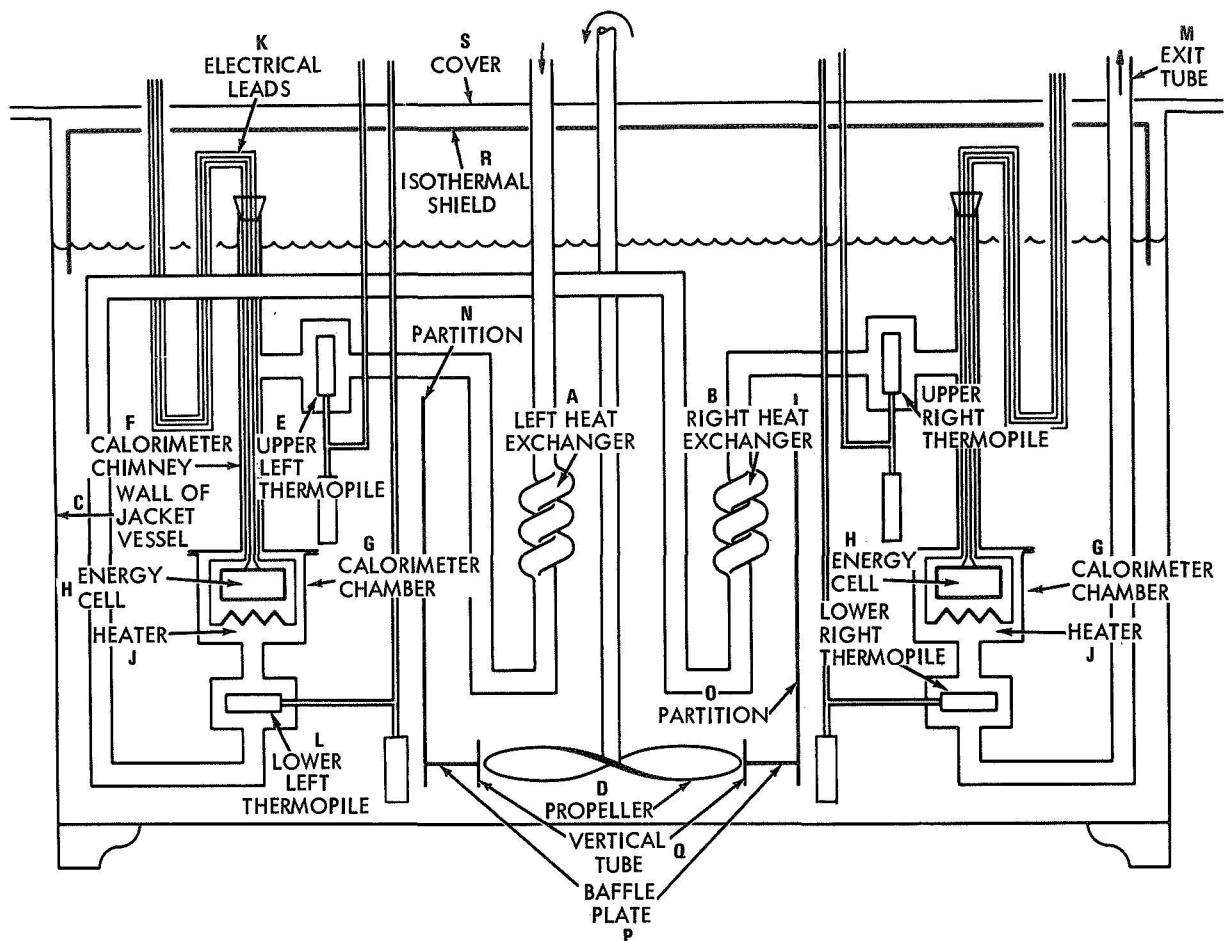


Figure 2. Jacket Vessel and Contents. A-left heat exchanger; B-right heat exchanger; C-wall of jacket vessel; D-propeller; E-upper left thermopile; F-calorimeter chimney; G-calorimeter chamber; H-energy cell; J-heater; K-electrical leads; L-lower left thermopile; M-exit tube; N-partition; O-partition; P-baffle plate; Q-Q-vertical tube; R-isothermal shield; S-cover.

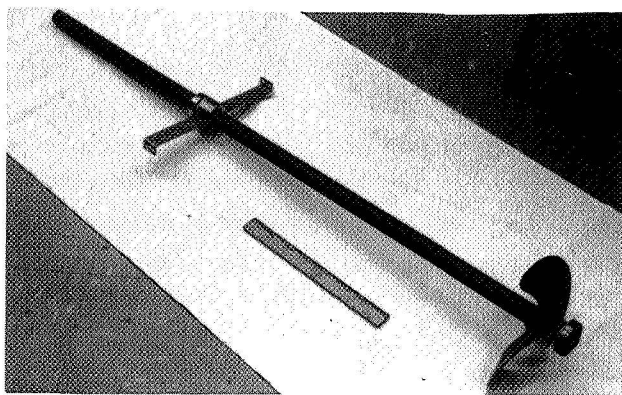


Figure 3. Propeller Assembly.

3-in (7.5 cm) air space at the top, the jacket-vessel is filled with water. Two stainless steel partitions, N and O, extending from the front of the vessel to the back, divide the interior into three compartments, each of which is a foot by a foot (30.5 cm  $\times$  30.5 cm) in cross section, and 4 ft (122 cm) high.

A horizontal baffle plate P fills the cross section of the central compartment except from a vertical tube Q which is approximately 3.5 in (9 cm) long and about 10.25 in (26 cm) in inside diameter. A three-blade, 10 in (25.4 cm) diam-

eter propeller D (g) is surrounded by this tube and when rotated, causes the water to move upward in the central compartment and downward in the two outer compartments. The propeller is driven

at 175 rpm by a 1/4 H.P. (186 W) electric motor with an integral speed reducer (h). The motor is electrically isolated from the rest of the system. Figure 3 is a photograph of the propeller assembly including the plastic shaft, two bearings, and a bearing support bracket.

The jacket vessel has two covers, both of which are represented in Figure 2 as R and S. The lower cover R, referred to as an isothermal shield, takes the form of an inverted rectangular cup fabricated from 0.25 in (6.2 mm) aluminum sheet. The rim or skirt of this shield extends down into the water to a depth of several inches (2.54 cm/in.) on all four sides and thus the entire shield plus the air enclosed by it are close to water temperature. The shield has the holes needed to permit the passage of various items such as the stirrer shaft and electrical leads and is divided into two symmetrical halves, the division passing through the holes, to facilitate assembly of the system.

The upper cover S is made from 0.0625 in (1.6 mm) stainless steel sheet. It is similarly perforated and split and serves to protect the isothermal shield from gross thermal disturbances such as might be caused by heat exchange between the shield and the room air.

Air is passed into the calorimeter from the air supply system via a maze of stainless steel tubing which is welded to the outer bottom surface of the jacket-vessel. A small section of this tubing is visible at A in Figure 1.

This maze causes the air stream to come into approximate thermal equilibrium with the water, and thereby reduces the thermal disturbance caused by the air when it passes into the jacket-vessel. This is explained more fully under "Discussion of Errors."

From this preliminary heat exchange the air flows up through a channel B (Figure 1) welded to the outside surface of the jacket-vessel and then, after passing through the jacket-vessel wall at C, enters the first of the two main heat exchangers. The latter is shown diagrammatically as A in Figure 2 and pictorially in Figure 4. It contains about 60 ft (20 meters) of 0.75 in (1.9 cm) inner diameter copper tubing.

B. Thermopiles - From this heat exchanger, the air stream enters the assembly shown in Figure 5 via the flanged opening A. This photograph shows three major components - a calorimeter chamber B and the exposed parts of two thermopiles, C and D. Each thermopile contains ten copper-constantan couples (twenty junctions) and each thermopile is used to measure the temperature difference between the air stream at points E and F and the cold-

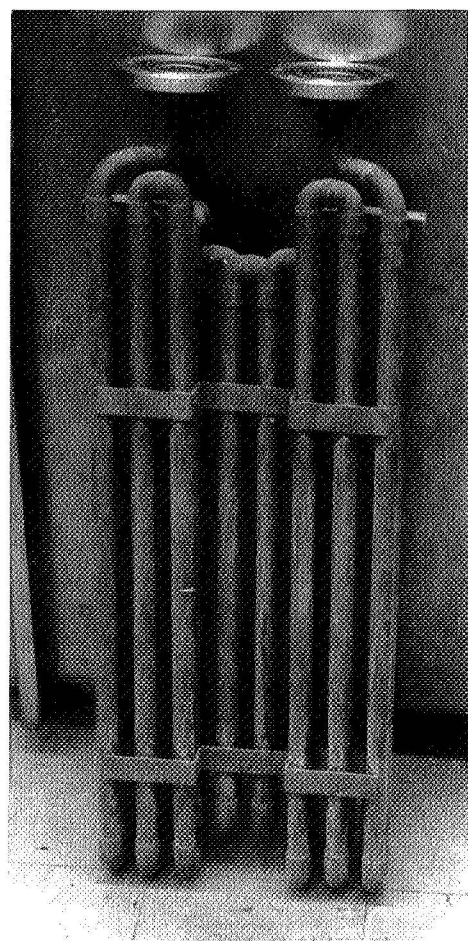


Figure 4. Heat Exchanger.



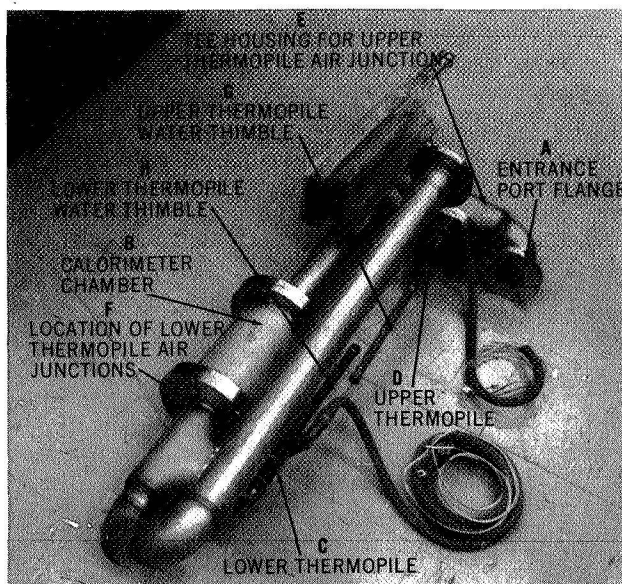


Figure 5. Chamber-Thermopiles-Leads Assembly. A-entrance port flange; B-calorimeter chamber; C-lower thermopile; D-upper thermopile; E-tee housing for upper thermopile air junctions; F-location of lower thermopile air junctions; G-upper thermopile water thimble; H-lower thermopile water thimble.

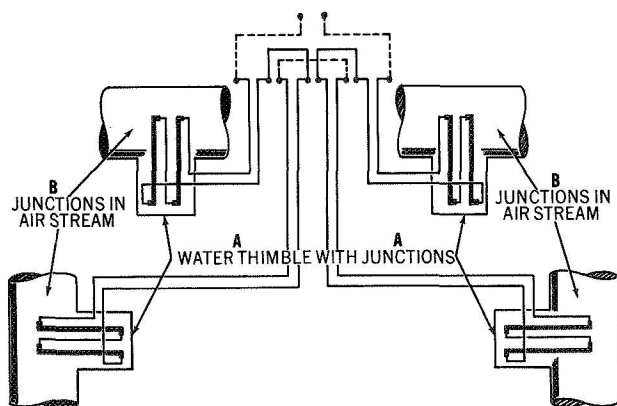


Figure 6. Thermopile Circuit Diagram. A-A — water thimble with junctions; B-B junctions in air stream.

being tied in a bundle, are passed into copper thimble B. The two copper terminal wires C are encased in braided shielding D and then passed through a rubber tube E, which terminates above the top of the jacket vessel. The support frame A in combination with the baffle plate F effectively fill the inner cross section of the tee E (Figure 5) which encloses them. Essentially all of the air stream must therefore pass through the lacing-filled opening, and over the bare junctions. The

fingers or thimbles immersed in the water at points G and H, respectively. In use, these two thermopiles are connected opposed as shown in either the left or right half of Figure 6. (For clarity each thermopile is depicted with only two couples instead of ten.) With this arrangement the net electrical output of the two thermopiles is independent of water temperature, and proportional to the change in temperature of the air stream caused by its passage through the calorimeter chamber. It would of course be possible to achieve the same end more simply by using a single thermopile with one set of junctions in the air stream at E of Figure 5 and the other at F, sensing respectively the air temperature before and after its passage through the calorimeter chamber B. The reason for the present arrangement is given in "Discussion of Errors."

The first or upper thermopile support fixture (D, Figure 5) is shown in Figure 7 as it appears when removed from the assembly. The Brown and Sharpe number-24-gauge copper and constantan thermocouple wires are both insulated with color-coded plastic and were purchased in duplex form, i.e., weakly joined along their lengths by a plastic-to-plastic bond. Such duplex wire facilitates the thermopile fabrication process. The junctions are formed by twisting together and then soft-soldering the bared ends of the copper and constantan wires. The ten junctions which are exposed to the air stream are left bare and can be seen in Figure 7 tied with linen thread to the nylon monofilament lacing of the support frame A. The junctions which remain at water temperature are first insulated with shrink tubing and then, after

white substance visible at G, (Figure 7) is a synthetic polymer which was used to seal the opening where the wires enter the thermopile support fixture. Without this seal, a portion of the air stream would leak around the wires and escape to the room via the rubber tubing E.

The temperature of the air as it passes from the calorimeter chamber is sensed by the lower thermopile. The thimble of this lower thermopile is visible at H in Figure 5. Figure 8 depicts this thermopile bolted in place in the apparatus but with the chamber walls and the upper part of the Figure 5 assembly removed. This same thermopile is shown separately in Figure 9.

In the original design of the calorimeter, the upper and lower thermopile support fixtures were essentially identical. Experimental results showed, however, that the junction support scheme depicted in Figure 7, while satisfactory for an upper thermopile, introduced significant errors if employed for a lower thermopile. This topic is covered more fully in "Discussion of Errors." Very briefly, the initial design was modified to improve the thermal contact between the air and the junctions at one end, and between the water and the junctions at the other.

Two modifications were made at the water end. First, after they were formed by twisting and soldering, the ten junctions were divided into five groups containing one pair each. Five sections of shrink tubing were then cut, each about twice the length of a thimble. Each such section was then bent double and one member of a junction pair was then passed into each end of the shrink tubing until the two bare junction tips almost met the center of the tubing. This process was repeated for each of the four pairs. The tubing sections were then shrunk around the wires. The five covered pairs of junctions were then positioned inside the thimble and finally, the latter was filled with molten Wood's metal.

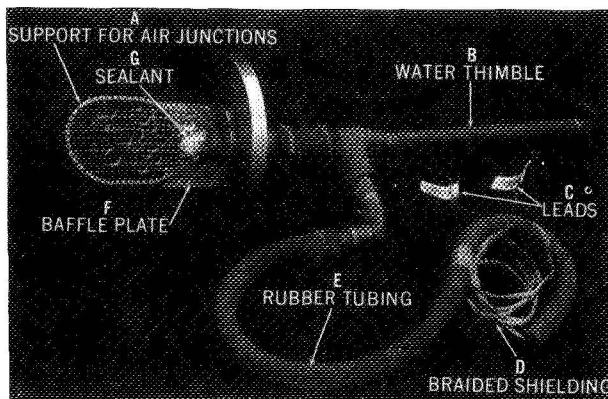


Figure 7. Upper Thermopile Assembly. A-support frame for air junctions; B-water thimble; C-leads; D-braided shielding; E-rubber tubing; F-baffle plate; G-sealant.



Figure 8. Attached View of Lower Thermopile Assembly. A-flanged opening; B-lower thermopile junctions; C-foam rubber ring.



The first step in fabricating the support fixture for the air end of the lower thermopile was to assemble the device shown at A in Figure 9. Two brass discs, B and C, each about 1.5 in (38 mm) in diameter, were perforated with twenty closely spaced holes, each about 0.2 in (5.1 mm) in diameter. Twenty 4.5 in (11.4 cm) lengths were cut from an equal number of 0.2 in (5.1 mm) diameter plastic drinking straws. The plastic straws were then passed through the holes in the brass plates and cemented in place to form the assembly illustrated.

The ends of the ten duplex thermocouple wires were separated for a distance of 21.5 in (55 cm) and each of the twenty ends thus formed was stripped of its insulation from its tip back for a distance of 21 in (53 cm), thus leaving a 0.5 in (13 mm) length separated but still insulated. Each of the twenty bared ends was coiled tightly around a 0.125 in (3.17 mm) rod, leaving uncoiled a 1 in (25 mm) tip. The twenty helical coils thus formed were stretched so that when they were passed into one end of the drinking straw assembly the uncoiled wire tips would protrude from the other. The two individual coils from any given duplex wire were passed through pairs of adjacent straws. The ten junctions could therefore be formed by twisting together and soldering the wire ends protruding from these same paired straws.

The finished soda straw assembly with its junctions was passed through the opening covered by the flange at A in Figure 8, and was then positioned in the tube which acts as an exit port for the air stream as it leaves the calorimeter chamber. The straw ends with their junctions can be seen protruding slightly from this port at B in Figure 8. Several foam rubber rings were wedged between the assembly and the exit tube which surrounds it. The uppermost ring can be seen as C of Figure 8. These served to hold the assembly in place and, in addition, acted as a seal, forcing the air stream to pass through the straws rather than around the assembly.

The sensitivity of the thermopiles can be computed approximately from the number of junctions and the thermoelectric force of the copper-constantan couple, thus

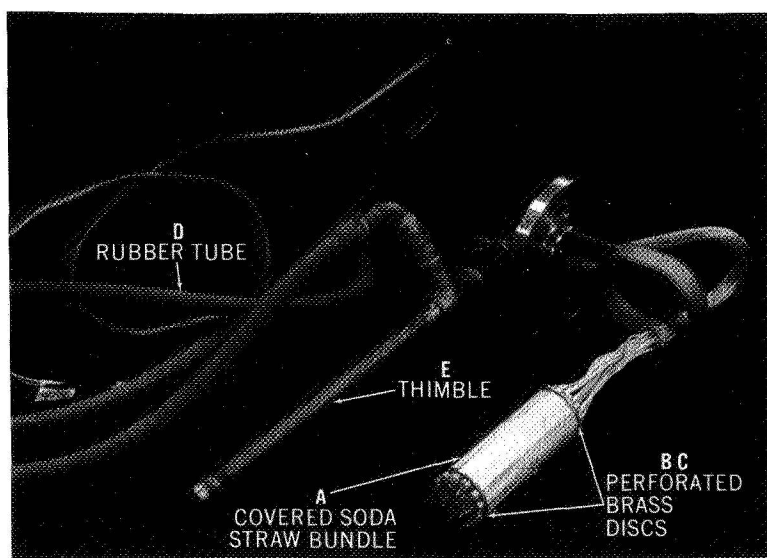


Figure 9. Lower Thermopile Assembly. A-covered soda straw bundle; B,C-perforated brass discs; D-rubber tube; E-thimble. .

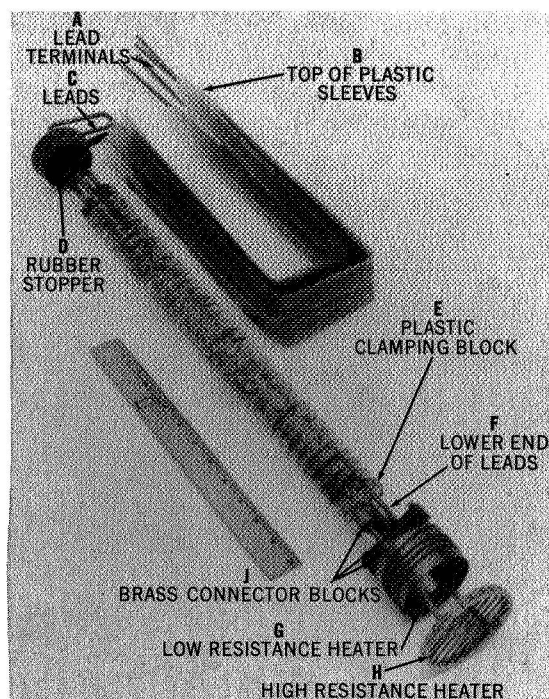


Figure 10. Lead Assembly with Heaters. A-lead terminals; B-top of plastic sleeves; C-leads; D-rubber stopper; E-plastic clamping block; F-lower end of leads; G-low resistance heater; H-high resistance heater; J-brass connector blocks.

$$10 \times 40 \text{ microvolts/degree} = 400 \text{ microvolts/degree.}$$

C. The Electrical Leads – The electrical leads are represented diagrammatically as K in Figure 2. Removed from the system they appear as in Figure 10. This apparatus has two design features which serve to minimize the serious errors which would otherwise be caused by the heavy leads needed in a calorimeter used for electrochemical studies.

The first such feature is visible in the upper right portion of the figure. Its purpose is to equilibrate the leads with the water before they enter the calorimeter chimney, thus minimizing the uncertainty caused by heat transport along the leads between the room air and the calorimeter air stream. The four outer lead terminals at A are 0.1875 in (4.8 mm) diameter round copper rods. At B, each of these enters a thin-walled plastic (PVC) sleeve where it is brazed to a copper strip that is 0.0625 (1.6 mm) thick and 1.0 in (25 mm) wide. In use, the upper two inches (51 mm) of these sleeves extend into the air space between the water and the isothermal shield. The lower part of each sleeve is immersed. The four copper strips terminate inside the sleeves about two inches (51 mm) below the upper left opening in the sleeves. The four 0.1875 in (4.8 mm) diameter rods C are also attached to the strips by brazing. These pass through the rubber stopper D and then down the chimney and into the calorimeter chamber. The object at E is a plastic clamp or spacer which holds the four rods in position. It fits the inside of the chimney at its lower terminus. When positioned in the apparatus, the extensions of the rods below this clamp are inside the calorimeter chamber.

Inside the calorimeter chimney, i.e., from the rubber stopper down to the plastic clamp, the leads are equipped with fins or vanes which aid heat exchange between the leads and the descending

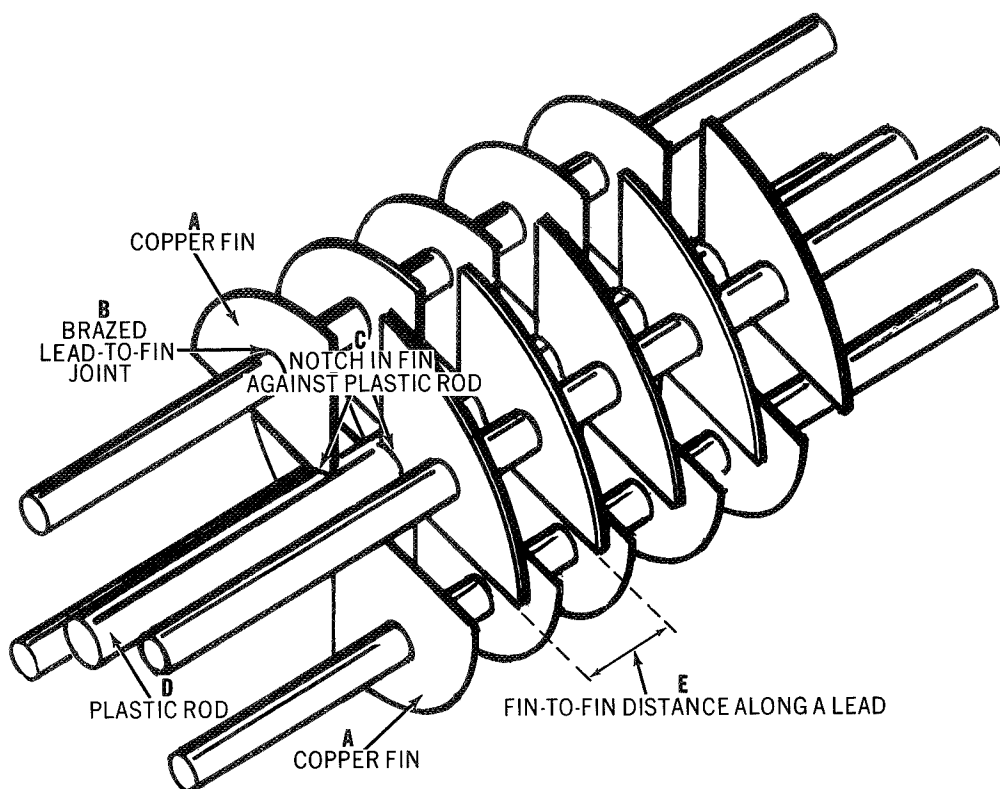


Figure 11. Finned Lead Assembly. A-copper fin; B-brazed lead-to-fin joint; C-notch in fin against plastic rod; D-plastic rod; E-fin-to-fin distance along a lead.

stream of air. The overall appearance of this part of the lead assembly is shown in Figure 10. The details of its construction are represented diagrammatically in Figure 11. Referring to the latter figure, the individual copper fins A are about 0.03 in (0.76 mm) thick and are brazed to the leads at B. A length of heavy waxed twine (not shown) is wrapped tightly around the leads, forcing the notches C in the fins against the 0.25 in (6.4 mm) diameter plastic rod D. The fin-to-fin spacing on a given lead rod E is 0.5 in (13 mm), and the overall diameter approximately equals the inside diameter of the chimney with its foam rubber lining. Two features of this assembly are important: the first is the relatively large area of the metal-air interface; the second is the fin arrangement which causes the air stream to divide and impinge on the fins at 0.25 in (13 mm) intervals along the entire 17 in (43 cm) length of the finned portion of the assembly.

**D. Calorimeter Chamber** – Each calorimeter chamber B (Figure 5) is a cylindrical, stainless steel enclosure having an inside diameter of about 4.8 in (12.2 cm) and a length of about 7 in (17.8 cm). The entire inner surface – sides, top, and bottom – is lined with 0.25 in (0.62 cm) thick foamed (poly) urethane rubber. The experiments described in this report were all performed with the four lead terminals F (Figure 10) attached to two heaters, G and H. These heaters are shown separately at A and B in Figure 12. The two heavy (0.1875 in., 0.48 cm) copper rods seen extending upward from each heater acted as mechanical supports and electrical terminals. The four heater terminals in each chamber were connected to the four lead terminals extending into that chamber by means of four especially-designed brass fixtures (C, Figure 12 and J, Figure 10) using setscrews.

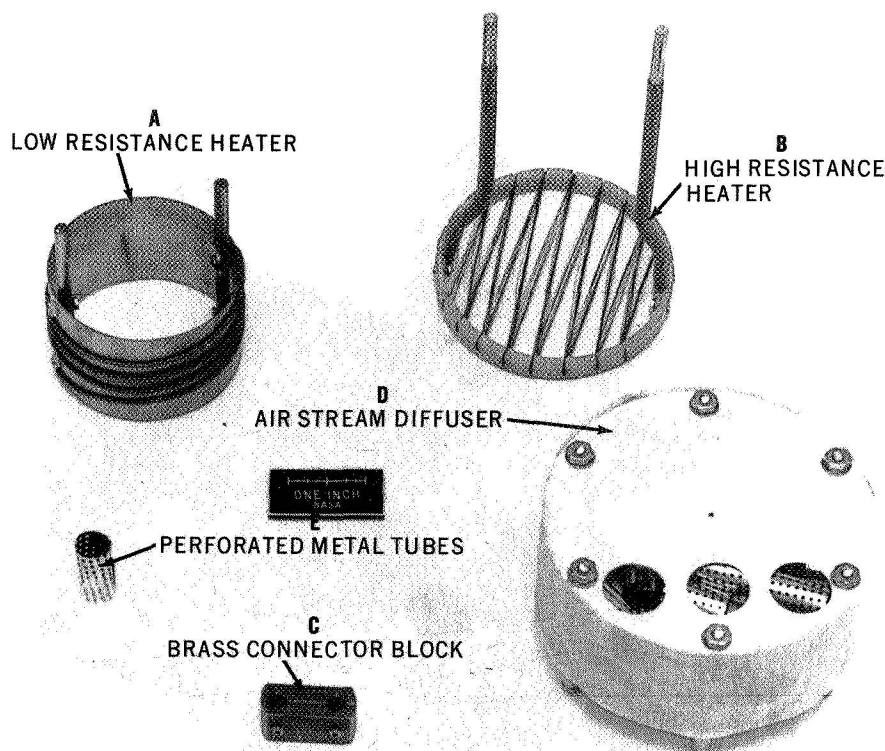


Figure 12. Miscellaneous Parts. A-low resistance heater; B-high resistance heater; C-brass connector block; D-air stream diffuser, E-perforated metal tubes.

Air flow through the calorimeter chamber is laminar, and, as a consequence, that portion of the stream which is heated by the electrical heaters has little or no tendency to mix spontaneously with the remainder of the stream but, instead, tends to preserve its identity as it passes down and out of the calorimeter chamber and over the lower thermopile junctions. It follows that the thermopile output would depend in a highly unpredictable way on the thermal pattern of the air stream and the way this pattern is related to the more or less discrete positions of the junctions.

This source of uncertainty was eliminated by intermixing the various portions of the air stream by means of the device depicted at D in Figure 12 and in Figure 13. This device was placed at the bottom of the calorimeter chamber where it essentially filled the chamber's cross section and served to break up the thermal strata or streamers previously referred to.

The design theory and construction details are evident in Figure 13. The four cardboard disks A are secured and spaced at 0.5 in (1.3 cm) intervals by the bolts B and the tubular spacers C. The three 0.75 in (1.9 cm) holes in the top disc D are rotated 120 degrees with respect to the corresponding three holes in the disc immediately below. This rotated placement is continued in the third and fourth discs. The short lengths of perforated, thin-walled metal tubing E are packed randomly in the spaces between the cardboard discs. (Figure 12, E is a photograph of one of these tubes.) The structure is enclosed and the tubes held in place by means of adhesive-coated paper tape as shown in Figure 12, D.

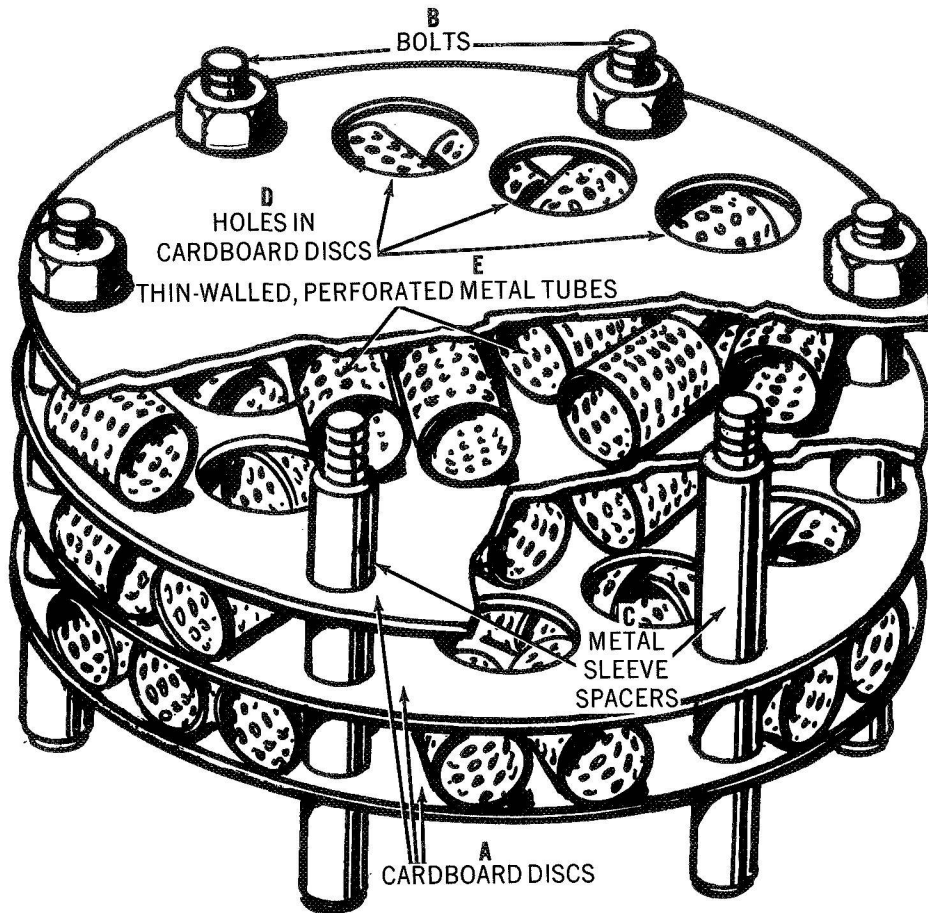


Figure 13. Air Stream Diffuser. A-cardboard discs; B-bolts; C-metal sleeve spacers; D-bolts in cardboard discs; E-thin-walled, perforated metal tubes.

#### 4. The Feedback Control System

The various elements of the feedback control system are mounted in the rack which can be seen adjacent to the calorimeter in Figure 1. Shown at D is the null detector (i) which amplifies the thermopile output. The resultant signal is conditioned by the recorder-controller 'E (j) and then used to regulate the DC power supply shown at F. The output of the latter goes to a heater in one of the calorimeter chambers. A heater in the other chamber is operated by the DC power supply G. The small power supply H can be ignored.

The thermocouple lead wires terminate in copper spade lugs which are crimped in place. To connect these leads to each other and/or to the null detector input, two or more of these lugs are placed together on a threaded nylon stud and forced together using a plastic nut. The absence of solder and all other metals except copper essentially eliminates thermal EMF's. The four pairs of thermocouple leads and the detector input cable are all shielded, and contacting surfaces are cleaned periodically.

The null detector has a center-zero meter which indicates the magnitude and sign of the input signal. The sensitivity of this device can be varied stepwise from plus or minus 30 nanovolts (nV)

full scale to plus or minus 100 millivolts (mV) full scale. The output of the detector is proportional to the meter reading and has the same polarity. The strip chart recorder is also a center-zero instrument. Its purpose is to afford a permanent record of the detector output.

The controller characteristics "proportional band," "reset," etc., can be varied over a wide range to meet the needs of a particular feedback situation. Control of the system was in most instances automatic. When desired a function switch on the controller made it possible to balance the system manually.

## 5. Data Acquisition System

The data acquisition system can be seen in the left rack in Figure 1. It was purchased as a unit and is comprised of the usual combination of clock J, scanner K, voltmeter L, and printer M. The clock is driven by the output of a quartz crystal oscillator or frequency standard N instead of depending on the 60-Hz line frequency.

All the components of the data acquisition system have an accuracy of 0.01% or better. Currents are measured as the voltage across an appropriately sized standard resistor, using four-wire connections. The data points included a standard cell and a short circuit. These are scanned intermittently to check the voltmeter calibration.

## IV. DESCRIPTION OF EXPERIMENTS

All the experiments which have been performed with the calorimetric system were designed to reveal its characteristics, to test its accuracy, and to identify the design weaknesses that were contributing to the observed errors. This effort ordinarily conformed to the following pattern. The first step was comprised of a series of experiments, drawn from those described below. Second, the results were analyzed in an attempt to determine what changes were needed. Third, these changes were implemented, and fourth, a second series of experiments was performed to evaluate the effect of the changes.

Initial experiments disclosed a severe system instability. These experiments were performed with air passing through the calorimeter and without any heat being dissipated in either chamber. The thermopiles were connected to the detector either individually or opposed as shown in Figure 6. All these experiments were characterized by violent fluctuations in the detector input.

This instability was eventually traced to three sources. The major source was a periodic fluctuation in the humidity of the air stream. This problem was eliminated by installing the drier. A secondary source was the relatively ineffective type of heat exchanger then being used. Installation of the copper heat exchangers previously described eliminated this problem. It was never thoroughly established but it seems likely that a small part of the instability was caused by small variations in the air flow rate. It is certainly true that such variations, if they were then present, would have caused corresponding fluctuations in thermopile output. In any event, the single air pressure regulator which was then being used in the air supply train was replaced by two series connected regulators.

It has been found that the calorimeter can be forced into a condition of unstable operation by using a low rate of air flow, 1 cu ft/min (28.3 liters/min), in combination with a relatively large heat input, about one watt or more in each chamber. This phenomenon is treated under "Discussion of Errors." This is the only significant instability in the system in its present form.

With the stability problem solved it was found that there were system asymmetries and that, as a consequence, a null thermopile output was obtained with different rates of heat dissipation in the two chambers. The following series of operations was ordinarily followed in making the determination.

First, the system is brought to an equilibrium or steady state condition with the stirrer running, the heaters open-circuited, and no air flowing. All four heaters and all four thermopiles are tested for continuity, for shorts to each other, and for shorts to the jacket vessel. The latter should be checked to be sure it is grounded and electrically isolated from both the stirrer motor and the air supply system.

After the null detector has warmed to its normal operating temperature, its input terminal is shorted using a plug designed for this purpose by the manufacturer of the detector. With the selector switch set on a relatively sensitive range, e.g.,  $1\mu\text{V}$  full scale, the detector is adjusted to a zero output as indicated by the zero center meter which is an integral part of the device. If necessary, the strip chart recorder is also adjusted to center zero.

Each thermopile is connected in turn to the detector input, and the magnitude and polarity of its output are recorded. Typically, each of these readings will be a few tenths of a microvolt (about  $0.001^\circ\text{C}$ ) and all of the same polarity.

The air supply is now turned on and the flow adjusted to one of the four rates which were employed in essentially all the experiments performed: 1, 2, 3, or 4 cu. ft/min (28.3, 56.6, 85.0 or 113 liters/min).

After a wait of about 15 minutes, the system again reaches a steady state and the individual outputs of the thermopiles are again measured. It is to be expected that these outputs will again be in tenths of a microvolt although at the higher rates of flow, readings in excess of  $1\mu\text{V}$  are not uncommon.

The four thermopiles are now connected as shown in Figure 6. The measured net thermopile output (NTO) is in the tenths of a microvolt range and should agree with the algebraic sum of the individual values with an error no greater than  $0.1\mu\text{V}$ .

All of the operations described up to this point are checks on the system and, if desired, can be deleted. The first essential step in this type experiment is to adjust the NTO to zero. This is an arbitrary and false zero which is necessitated by asymmetries in the system. In theory, its use produces no error. The next operation is to energize a heater in one of the calorimeter chambers using as a source the power supply shown in G in Figure 1. At essentially the same time one of the heaters in the other calorimeter chamber is energized to approximately the same power level using the feedback control circuit. Either the manual or automatic control mode can be used during

this start-up phase, but time will ordinarily be saved if manual control is used for the first few minutes, after which the system can be placed on automatic control. When the system is balanced and in a steady state the selected data points are scanned using the data acquisition system. These points will of course include the current and voltage of each of the two heaters since the immediate objective of the experiment is to determine the degree of agreement between the two heater wattages.

The above test of system accuracy was varied by changing the air flow rate and by changing the amount of power supplied to the heaters. These experiments were performed using the two low resistance heaters, the two high resistance heaters, or a high resistance heater on one side in combination with a low resistance heater on the other. Initial system tests such as these revealed that accuracy was markedly dependent on test conditions, the wattage difference on the two sides varying from a few tenths of one percent at one extreme to 20 percent at the other. Errors in the range of 5 to 10 percent were most common.

The results of these tests were analyzed in an attempt to identify the source of the error. Other types of experiments were performed with the same objective. For example, numerous sensitivity determinations were made by measuring the temperature rise of the air stream caused by a given heater wattage. The observed value was then compared with the theoretical sensitivity which was computed from the air flow rate, the thermopile sensitivity, and the molar heat capacity of air. The effectiveness of the heat exchangers was evaluated by heating the incoming air stream to about 60°C (333K) and observing the resulting change in the output of the top thermopile on the input side. On several occasions system accuracy was evaluated under conditions of reverse flow, i.e., with the air stream passing first into the right heat exchanger and from there to the right chamber, the left heat exchanger, the left chamber and then out. The system was designed to facilitate this change.

In light of the preceeding it can be seen that only the final series of experiments is significant in the sense that it can be used to evaluate the system in its present form. The following is an account of this last set of measurements.

One of the first experiments in this group was a sensitivity determination. The first step was to bring the system to a steady state with the heaters open-circuited, the NTO set at zero, and an air flow rate of 2 cu ft/min (56.6 liters/min). The high resistance (373  $\Omega$ ) heater on the left side was then turned on at 20.03V and 0.0531A or 1.074W. About ten minutes later the NTO was stable at 276  $\mu$ V. The sensitivity is therefore 1.074 W/276  $\mu$ V or 3.9 mW/ $\mu$ V at 2 cu ft/min (56.6 liters/min). At a flow rate of 4 cu ft/min (113 liters/min) the corresponding figure would be  $3.9 \times 2 = 7.8$  mW/ $\mu$ V. Two other sensitivity determinations, made at 4 cu ft/min (113 liters/min) and heater wattages of 0.067 W and 0.013 W gave sensitivities of 7.2 and 8.4 mW/ $\mu$ V, respectively. In the experimental results that follow, a rounded figure of 8 mW/ $\mu$ V will be used for a flow of 4 cu ft/min (113 liters/min) and 4 mW/ $\mu$ V at 2 cu ft/min (56.6 liters/min).

The remaining experiments included in the final series were all accuracy determinations and are presented in Table 1. The numbers in the extreme left column correspond to the order in



Table 1  
Experimental Results

Experiment No.	Control Mode	Flow Rate (CFM)	Left Heater			Resistance	Right Heater			Error				
			Voltage (volts)	Current (milliamps)	Wattage (milliwatts)		Voltage (volts)	Current (milliamps)	Wattage (milliwatts)	Wattage (milliwatts)	Percentage (%)	Voltage (microvolts)	Temperature (deg. C $\times 10^{-3}$ )	
1	M	2	H	10.09	27.03	272.7	H	10.09	27.07	273.1	0.4	0.15	0.10	0.25
2	M	2	H	10.09	27.03	272.7	H	10.09	27.06	273.0	0.3	0.1	0.075	0.2
3	M	2	H	20.03	53.64	1074.4	H	20.05	53.80	1078.7	4.3	0.4	1.1	2.7
4	M	2	H	20.063	53.73	1078.0	H	20.053	53.80	1078.8	0.8	0.07	0.2	0.5
5	A	4	L	0.5662	500.6	283.4	H	10.097	27.09	273.5	9.9	3.5	1.1	2.8
6	A	4	H	6.325	16.94	107.1	H	6.345	17.03	108.0	0.9	0.8	0.1	0.28
7	A	4	H	1.987	5.323	10.58	H	1.968	5.282	10.39	0.19	1.8	0.024	0.06
8	A	4	H	1.987	5.323	10.58	H	1.973	5.310	10.48	0.10	0.95	0.012	0.03
9	A	4	H	0.5057	1.354	0.685	H	0.5147	1.370	0.705	0.02	2.9	0.0025	0.06
10	A	4	H	20.58	55.13	1135	H	20.64	55.44	1144	9.0	0.79	1.1	2.7
11	A	4	H	20.58	55.13	1135	H	21.615	55.34	1141	6.0	0.53	0.75	1.9
12	A	4	H	15.002	40.18	602.7	H	15.033	40.36	606.7	4.0	0.66	0.5	1.2
13	A	4	H	4.993	13.37	66.76	H	5.011	13.45	67.40	0.64	0.95	0.08	0.25
14	M	4	H	5.011	13.42	67.25	H	5.010	13.44	67.34	0.09	0.13	0.01	0.02
15	A	4	H	5.011	13.42	67.25	L	0.2723	251.2	68.40	1.15	1.7	0.14	0.35
16	A	4	H	5.012	13.42	67.26	L	0.2790	242.2	67.57	0.3	0.46	0.04	0.1
17	A	4	H	5.012	13.42	67.26	L	0.2802	249.8	69.99	2.7	4.0	0.3	0.75
18	A	4	H	5.012	13.42	67.26	L	0.2813	249.5	70.18	2.9	4.3	0.36	0.9
19	A	4	H	11.206	30.01	336.3	L	0.6322	556.3	351.7	15.4	4.6	1.9	4.8
20	A	4	H	16.082	43.08	692.8	L	0.9034	804.2	726.5	33.7	4.7	4.2	10.5

which the experiments were performed. When similar experiments are listed consecutively it means that after an initial set of data was taken the system was permitted to continue to operate under steady state conditions for perhaps another 10 or 15 minutes to permit observation of system stability and to assure a valid balance. The second set of data was recorded after this period.

In the second column the control mode is given as either automatic (A) or manual (M). The third column gives the heater resistance in the left chamber as either high (H) or low (L). The actual resistances were  $373\ \Omega$  and  $1.1\ \Omega$ , respectively. The output of the heater in the right chamber varies in response to action by the controller. The voltages and currents listed for that side were therefore obtained as an average of four or more scans by the data acquisition system. System stability was such that this variation was small relative to the error. Because of this a sigma value for the wattage uncertainty was not computed.

The error is the difference between the two measured wattages. This is expressed in Table 1 as an absolute value in milliwatts, as a percentage, and in terms of a discrepancy in the NTO in  $\mu\text{V}$ . This latter quantity must take into account system sensitivity, which is dependent on air flow rate. Thus, as given above, at 2 cu ft/min (56.6 liters/min) sensitivity is  $4\ \text{mW}/\mu\text{V}$ , and at 4 cu ft/min (113.2 liters/min) it is  $8\ \text{mW}/\mu\text{V}$ . In the last column the error in microvolts is expressed as an equivalent temperature error using the relation

$$\begin{aligned} 1\ \mu\text{V} &= 2.5 \times 10^{-3}\ ^\circ\text{C} \\ &= 2.5 \times 10^{-3}\ \text{K}. \end{aligned}$$

Figures 14 and 15 are included to illustrate some of the dynamic characteristics of the system. These figures are both tracings of the original ink line on the recorder chart. Each is thus a

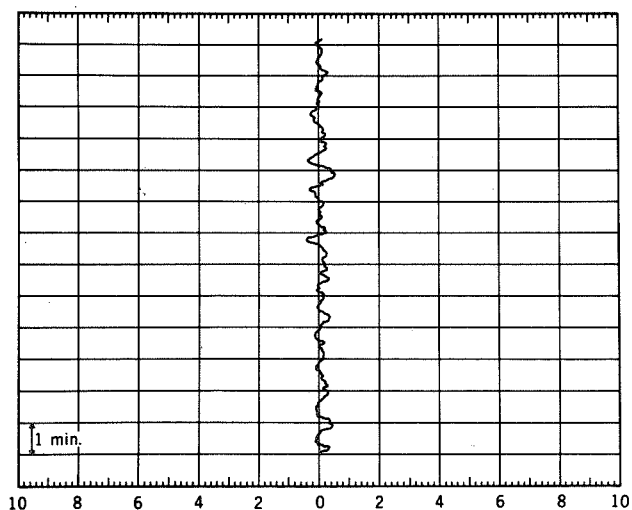


Figure 14. Recorder Chart, Showing Control Stability

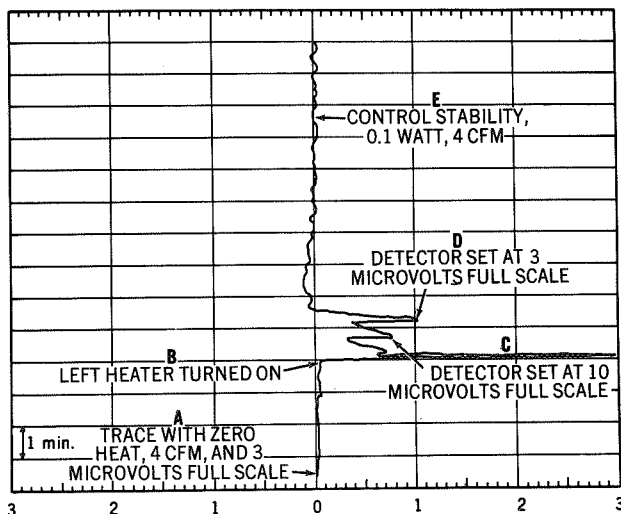


Figure 15. Recorder Chart, Showing Control Characteristics. A-trace with zero heat, 4 cu ft/min (113 liters/min), and 3 microvolts ( $\mu\text{V}$ ) full scale; B-left heater turned on; C-detector set at  $10\ \mu\text{V}$  full scale; D-detector set at 3 microvolts full scale; E-control stability, 0.1 watt, 4 cu ft/min (113 liters/min).

graphical record of the NTO as a function of time. Detector sensitivity was set at either  $3\ \mu\text{V}$  (Figure 15) or  $10\ \mu\text{V}$  (Figure 14) full scale.

Figure 14 is indicative of control stability under worst case conditions, i.e., maximum flow (4 cu ft/min) (113.2 liters/min) and maximum heat dissipation (1.1 W). Referring to Figure 15, the trace from A to B was made with no heat being dissipated in either chamber and with a flow of 4 cu ft/min (113.2 liters/min). It can be seen that the short-term uncertainty or system "noise" is approximately  $0.01\ \mu\text{V}$  under these conditions. At B, 6 V was applied across the high resistance heater on the left side, thus unbalancing the system and causing the indicator to go off scale. The gain of the detector was reduced to return the indicator to the scale, and then was increased to  $10\ \mu\text{V}$  full scale at C and finally to  $3\ \mu\text{V}$  full scale at D. At E the automatic controller had re-balanced the system and the data given under experiment six of Table 1 was recorded.

## V. DISCUSSION OF ERRORS

The calorimetric system described in this report is simple in concept but it is nonetheless a complex device in the sense that there are numerous possible sources of error, some of which are not immediately apparent. Work to date has been devoted exclusively to identifying and eliminating such defects. The most recent experimental results, with particular reference to the data in Table 1, show that the system still has flaws which are causing error. Thus, in a sense, this is an interim or status report.

The primary purpose of this section is to analyze these most recent findings with the objective of identifying the sources of errors. This discussion would not be complete, however, without mentioning two other types of system weakness – those which were avoided in the original design, and those eliminated by system modifications. The topics enumerated below include all three categories.

### 1. Water Bath and Jacket Vessel

The jacket vessel design with its three compartments and a large volume of gently stirred water seems to be very effective in affording, first, an environment that is essentially free of thermal gradients, and second, a bath temperature which changes very slowly with time.

The preliminary heat exchanger on the outer bottom surface of the jacket vessel was included in the original design in order to minimize the thermal gradients in the water which surrounds the thermopile thimbles and other sensitive parts of the system. With the present design most of the thermal disturbance caused by the incoming air stream is confined to water near the bottom of the jacket vessel. The resulting gradients and striations tend to be destroyed by the propeller action before they get to the more sensitive parts of the system.

A water bath temperature that is changing too rapidly can cause error because of thermal lags in the system. Such lags were detected in the present system as significant thermopile outputs even though the heaters were not being operated. In the case of measurements made at or near room temperature, such as those reported here, there is evidence that it would be desirable to

insulate the outer surfaces of the jacket vessel. If measurements were to be made at elevated or depressed temperatures, e.g., 40°C (313K) or -10°C (263K) such insulation would probably be essential. It should be mentioned that the addition of a little antifreeze to the water would be a good idea, too.

## 2. Electrical Leads

The electrical leads in a calorimeter of this type can cause error in at least five different ways. None of these are believed to have contributed significantly to the errors reported in Table 1 but all are discussed here because a modified design or a different usage could greatly magnify one or more of those problems.

When relatively large currents are used, the joule heat dissipated by the leads can represent a significant proportion of the total heat dissipated on a given side of the calorimeter. Even if it is assumed that all this heat is picked up by the air stream, i.e., that none is lost from the system via the leads, the electrical power which produces this heat must nonetheless be included in the power balance. In practice this means that the voltage of a heater, for example, must be measured at some point near the top of the chimney and that the term "calorimeter chamber" is technically a misnomer if it does not include the chimney. In our apparatus the voltage terminals were connected to the current leads immediately above the rubber stopper.

A section of each lead was formed into a loop which was immersed in the water (Figure 10). The purpose of this arrangement was to isolate thermally the calorimeter from the room air. The effectiveness of the design parameters chosen could have been evaluated by heating that portion of the leads which extends into the room to a moderately high temperature such as 60° to 80°C (333K to 353K) and observing the resultant change in the output of the lower thermopile. This very simple test was overlooked. An analysis of Table 1, however, seems to exclude room temperature effects as a major source of error.

At the point where they pass through the rubber stopper, the leads tend to have a temperature above that of the water. This temperature difference causes heat to be lost from the calorimeter, and unless this loss is identical on the two sides, error will be produced. The gradient referred to has three sources. One of these sources, joule heating, has already been mentioned. Another source is the heater or the cell to which the leads are attached. In general, these devices are at a temperature that is above that of the air stream, and therefore they cause heat to flow up the chimney along the leads. The third and last phenomenon contributing to this error is the elevated temperature of the air stream surrounding the leads due to its diminished velocity after leaving the heat exchanger. This so-called "stagnation effect" is discussed in this section under "Heat Exchanger."

The leads used in the project had a diameter of 0.19 inch (0.48 cm) and an effective length within the chimney of about 20 inches (50 cm). When carrying one ampere, a pair of such leads dissipates about one milliwatt of heat. The 33.7-mW error observed for Experiment 20 (Table 1) quite obviously is not attributable to joule heating.

In a similar vein, using the same experiment as an example, it is unlikely that 4.7% of the heat from a heater could travel up such finned leads against a countercurrent stream of air.

In short, it is improbable that the observed errors are attributable either to joule heating or to the fact that the lower termini of the leads are at an elevated temperature.

If a calorimeter of this type were to be used in making measurements requiring large currents, the problem of joule heating would become more intractable and would have to be reexamined. It might be advantageous under such circumstances to adopt the following strategem. Let the heater on one side of the calorimeter, the right side, for example, have a large resistance so that joule heating of its leads will be negligible. The second pair of leads on this right side is connected to nothing inside the calorimeter chamber. Instead, a single lead passes down the chimney, bends into a 180° loop where it enters the calorimeter chamber, and then passes back up the chimney. The current to the electrochemical cell in the chamber on the left side of the system is passed through this dummy lead first. The purpose of this arrangement is to produce the same amount of lead heat on both sides of the calorimeter and thus eliminate the error. It would of course be necessary to monitor the voltage across the dummy leads and add the wattage to that of the heater.

### 3. Heat Exchangers

The heat exchangers are among the most critical components in a calorimeter of the type described here. This fact is made obvious by considering the consequences if the temperature of the air exhausting from the first heat exchanger is significantly different from that of the water. Relatively rapid changes in the air temperature, even though they conform to corresponding changes in water temperature, would be equally ruinous. It is indeed sobering to consider the data in Experiment 7 of Table 1 in terms of the requirements this experiment imposed on the heat exchangers. Here we see a 1.8% error with a temperature equivalent of only  $6 \times 10^{-5} \text{ }^{\circ}\text{C}$  ( $6 \times 10^{-5} \text{ K}$ ).

A second and what appears to be an equally stringent requirement is imposed on the exchangers by the so-called stagnation effect. This phenomenon can be expressed mathematically by the equation

$$MC_p T_0 = MC_p T_1 + \frac{MV^2}{2} ,$$

where M is the mass of the gas,  $C_p$  its molar heat capacity at constant pressure, T its temperature and V its velocity. This equation states that the energy of a moving mass of gas ( $MC_p T_0$ ) is equal to its static or rest energy ( $MC_p T_1$ ) plus its kinetic energy ( $MV^2/2$ ). In terms of the present problem this equation tells us that the gas stream, because it slows down on leaving the relatively small diameter exchanger, will undergo an isobaric, adiabatic rise in temperature. The heat exchanger in Figure 4 has an inside diameter of 0.75 in (1.9 cm). The effective diameter of the thermopile support frame (A in Figure 7) can be taken with sufficient accuracy as about 2 in (5.1 cm). Using these dimensions and a flow rate of 4 cu ft/min (113 liters/min), the above equation predicts an air temperature rise of  $0.017^{\circ}\text{C}$ . This is indeed a very large effect when compared with  $6 \times 10^{-5} \text{ }^{\circ}\text{C}$  ( $6 \times 10^{-5} \text{ K}$ ).

When viewed in the light of these constraints, heat exchanger design looms as a formidable and perhaps insurmountable problem. Such gloomy theoretical predictions, however, are not borne out by experimental results.

A stagnation effect of  $0.017^{\circ}\text{C}$  ( $0.017\text{K}$ ) corresponds to a thermopile output of  $0.017^{\circ}\text{C}/0.0025^{\circ}\text{C} \mu\text{V}^{-1}$  ( $0.017\text{K}/0.0025\text{K} \mu\text{V}^{-1}$ ) =  $6.7 \mu\text{V}$ . No such voltage was ever observed from a top thermopile on either side of the apparatus.

Fears with regard to the ability of the exchangers to equilibrate the temperature of the incoming air stream with the temperature of the water are equally groundless. The usual methods employed in heat exchange calculations predict that the air, as it exhausts from the exchanger on the inlet side, will have a temperature differing from that of the water by about  $0.001^{\circ}\text{C}$ . This difference was calculated by assuming a flow rate of 5 cu ft/min (141 liters min) and a  $1^{\circ}\text{C}$  (1K) difference between the air supply and water temperatures, but reasonable changes in these assumed values would not greatly alter the computed result. If during the course of an experiment, however, the sign of the air supply temperature were to change relative to that of the water, there would be a concomitant abrupt change of about one  $\mu\text{V}$  in the thermopile output. Such a change in the absence of a known cause was never observed.

It is not the purpose of this discussion to claim that none of the uncertainty in the present system is attributable to the heat exchangers. The intent here instead is to point out that predictions based on theory are unduly pessimistic, and to advise against any effort to improve heat exchangers until other more serious sources of error have been eliminated.

In a similar vein, it is not advocated here that the books on heat exchanger design be rewritten or that the preceeding equation dealing with stagnation be discarded. The heat exchanger equations referred to must include a film coefficient which is derived empirically under conditions of temperature head which exceed by orders of magnitude those which obtain in the present system. It is not surprising that such coefficients are not applicable.

The discrepancy between theory and observation is not so easily explained in the case of the stagnation effect. The experimental evidence supporting a negligible temperature rise appears to be incontrovertible. Yet if the air in the exchanger is close to water temperature, as previously indicated, what happens to the kinetic energy of this gas after it emerges? This matter should be investigated.

An unexplained and perhaps related phenomenon was observed. Abrupt changes in air flow rate were always accompanied by relatively large excursions in the output of the thermopiles. A cursory attempt to explain such observations in terms of stagnation effects was largely unsuccessful.

A similar attempt to explain the observed phenomena in terms of pressure gradients was equally unsuccessful. Toward this end the gas pressure within the system was measured at two different points and at different flow rates. The results of these measurements are presented in Table 2. One point was the inlet tube near where it connected with the preliminary heat exchanges on the bottom of the jacket vessel (point A, Table 2). The other point was the top of the left chimney with the air flow from left to right (point B, Table 2).

Table 2  
System Pressure Gradients

Flow Rate		Pressure			
cu ft/min	liters/min	A		B	
		psig	N/m <sup>2</sup>	psig	N/m <sup>2</sup>
1	28.3	0.09	620	0.06	413
2	56.6	0.31	2,140	0.23	1,590
3	85.0	0.64	4,410	0.49	3,380
4	113.2	1.13	7,790	0.85	5,860

#### 4. Thermopiles

The copper constantan thermocouple is a highly dependable device for the measurement of temperature differences. In some applications this couple must be calibrated to compensate for small batch-to-batch differences in the alloy and for non-linearity of output, but with the present mode of use – balancing the output of one thermopile against that of another – such calibration is unnecessary, and accuracy and dependability are correspondingly enhanced.

In spite of these very real advantages one must exercise certain precautions in the fabrication and use of thermopiles intended for the present application. For example, the junctions must be kept scrupulously clean and must not be touched with the bare fingers. The wires must not be kinked, stretched, or otherwise strained.

It is also advisable to fabricate the thermopiles in pairs. Then, as the lengths of wire are cut from the roll, these lengths can be alternated, one for one member of the pair and then one for the other member. In this way any difference between one end of the roll and the other is distributed equally between the pair members.

It was found that the initial design of the lower thermopiles was faulty in that the temperature of the air junctions was partially dependent on that of the water. Two factors contributed to this weakness. The first was the rather ineffective heat transfer between the bare junctions and the gently moving stream of air. The second was the relatively good thermal coupling between the water and the thermocouple wires where the latter was surrounded by sealant (G, Figure 7). The improved form of the lower thermopile support facilitates heat transfer between the junctions and the air stream by greatly increasing the area of the metal-air interface. At the same time the flow of heat from the water to the air junctions was impeded by removing the sealant from the position indicated in Figure 7 and, instead effecting a seal within the rubber tube (D, Figure 9). As a final improvement the axial flow of heat within the thimble (E, Figure 9) was facilitated by filling the voids with Wood's metal.

The use of excessively fine wire magnifies the fabrication problem and could lead to more serious difficulties such as a sluggish detector or excessive Johnson noise from the thermopile. The use of very thick wire, on the other hand, would increase the error caused by heat flow along the wires. The 24 gauge wire used in the present system represents a reasonable compromise.

## 5. Calorimeter Chamber

The most serious weakness of the calorimeter in its present form is in the design of the two calorimeter chambers. A significant fraction of the heat evolved is lost through the chamber walls, and when this loss is different on the two sides, the measurement is in error by the amount of this difference.

An approximate value for the fraction of heat which is lost can be obtained by comparing the calculated sensitivity of the system with the measured sensitivity. The former was found to be  $1.5 \text{ mW}/\mu\text{V}$  using the following quantities: the specific heat of air ( $0.25 \text{ cal/deg g}$ ), its density ( $1.2 \text{ g/L}$ ), the thermoelectric power of the ten-junction thermopiles ( $400 \mu\text{V/deg}$ ), and the air flow rate ( $1 \text{ cu ft/min}$ ) ( $28.3 \text{ liters/min}$ ). Because there is a loss of heat, the measured sensitivity will vary with conditions such as flow rate and the amount of power being dissipated, but the three sensitivity determinations made after the final modification of the system yielded values of 1.8, 1.9, and  $2.1 \text{ mW}/\mu\text{V}$ , all of which are normalized to a flow of  $1 \text{ cu ft/min}$  ( $28.3 \text{ liters/min}$ ). A comparison of these data with the calculated value of  $1.5 \text{ mW}/\mu\text{V}$  indicates that roughly 25 percent of the heat is lost through the chamber walls between the heat source and the lower thermopile junctions.

With such a large heat loss it is to be expected that the calorimeter would yield accurate results only if the heat sources on the two sides are essentially identical with regard to both their geometries and their positions in the calorimeter chambers, for only under these circumstances would there be similar thermal patterns in the air streams on the two sides and, as a consequence, similar rates of heat loss from the two chambers.

It follows from this discussion and from an examination of Figure 10 that experiments involving the same type heater on both sides should yield results which are more accurate than those entailing a low resistance heater on one side and a high resistance heater on the other.

The data in Table 1 are consistent with this conclusion. Note that with just two exceptions all the experiments with a high resistance heater on both sides were in error by less than 1%. Experiments 7 and 9 entailed the measurement of small amounts of power and as a consequence can be looked upon as tests of system stability. Indeed, the error in Experiment 9, 2.9%, can only be viewed as fortuitous since such an error implies a system stability of  $0.002 \mu\text{V}$ . The system is not that stable even over a short time span.

On the other hand, experiments involving a low resistance heater on one side and a high resistance heater on the other, Experiments 5 and 15 through 20, all had somewhat higher errors. The results of Experiments 15 and 16 appear to be exceptions but are of doubtful validity. Note that when this determination was continued to obtain a more characteristic steady state, the error as seen in Experiments 17 and 18 was much increased.

These data are qualitatively consistent with the hypothesis that the error is caused by loss of joule heat from the leads. As shown in the discussion of lead errors, however, the observed error is too large to be attributed to this source.



## 6. Data Acquisition and Feedback Control Systems

The data acquisition system was designed to yield a maximum error of 0.01 percent under all operating conditions. Intermittent calibration checks were made to maintain this level of accuracy. The data acquisition system can therefore be ignored as an error source.

The modern automatic controller has been perfected to the point where control accuracy rarely depends on controller quality. Almost invariably it depends instead on the inherent stability of the system being controlled, and on the skill of the operator in adjusting the compensating networks of the controller to match the transfer characteristics of that system. The findings of the present study are consistent with this generality. Most experiments were designed to evaluate system accuracy and were therefore made with a constant wattage being supplied to one of the heaters. The control problem was thus minimized and the control error was essentially zero. Numerous recorder traces showed maximum excursions of less than  $0.1 \mu\text{V}$ . The average or integrated deviation from the set point would of course be much less than this. A net thermopile output of  $0.1 \mu\text{V}$  corresponds to a temperature error of  $2.5 \times 10^{-4} ^\circ\text{C}$  ( $2.5 \times 10^{-4} \text{ K}$ ) and, at 28 liters/min, to a wattage unbalance of 0.3 mW. This would indicate that the uncertainty attributable to the controller would be in the hundredths of a milliwatt. Errors of this magnitude are of no concern with the system in its present state of development.

## VI. CONCLUSIONS

A brief consideration of the various projects described in Section II makes it abundantly obvious that a great deal of time, money, and effort has been devoted to the development of calorimeters which were designed for the study of energy cells. It is equally obvious that not one of these instruments has been tested experimentally to determine its capabilities, e.g., its range, the nature and magnitude of its errors, or how these errors are related to operating conditions. One or two of the calorimeters described were studied rather carefully when in the design phase but this, very definitely, is not good enough. The result of this situation is that the scientists and engineers who need these thermal data do not have them or, what is a great deal worse, they think they have them but don't. The indications are that one of these projects is based on a calorimeter with an error that can be as large as 40 percent, yet the data generated are used to compute reaction enthalpies to three significant figures.

It does seem to be time for a change.

In appraising this situation, several questions arise. One is, "What is needed?" Another is, "Of the various instruments that have been described, which are the most promising in terms of meeting these requirements?", and finally, "What is the present status and future potential of the AFTBC and what will be its role?". This section of the report is addressed to these questions.

Certainly one greatly needed device is an engineering type instrument of low cost and modest accuracy, perhaps with an error tolerance of 5%. This calorimeter should be convenient to work with and should be adaptable to a wide range of cell types and sizes. The AFTBC does not meet these requirements. It is expensive to construct; it will accommodate a relatively narrow range

of cell sizes; and because of the weight and complexity of its components, it is an arduous and time-consuming system to work with.

Two of the systems described in the "Literature Survey" are worth considering for such engineering-type measurements. It should be emphasized, however, that neither system has demonstrated the ability to meet even the modest accuracy requirements set forth above.

The S. Gross (Reference 14) design is the more promising of these two candidates. The design and size of the base plate of this instrument could be varied widely and inexpensively to meet the needs of almost any calorimetric task. For example, the base plate could consist of two halves, one clamped to each side of the cell. Alternatively, the base plate could closely simulate the heat sink to which the cell is to be attached in a space vehicle or other application. This could be an important advantage. There is no obvious reason why a large battery of cells could not be treated similarly.

An apparent weakness of the Gross instrument, its failure to compensate for joule heating of the leads, could perhaps be eliminated by splitting the base plate into two parts which are electrically isolated from each other but in good thermal contact. Then the copper inlet and outlet tubes could serve also as electrical leads to the cell or battery.

The heat leak error could almost certainly be held to an acceptable level. For example, one could evaluate the error and correct for it. Operation in a vacuum chamber while using suitable radiation shields is an alternative solution. Perhaps it would be advantageous to completely surround the cell with the "base plate."

A final advantage of the Gross design is the interchangeability of all the system components other than the base plate. The pump, data acquisition system, and detector circuit could all be designed to accommodate anything from a small cell to a large battery. A new task would need only a new base plate, an inexpensive requirement.

A possible alternative to the Gross design is that being developed by Johnston (Reference 8). In the absence of experimental proof to the contrary, however, the former seems to be the more attractive. One weakness in the Johnston instrument is described in Section II. This criticism is of questionable validity if applied to an instrument that is to be used to obtain engineering data. It was not mentioned that there is no compensation for joule heating of the leads. In the prototype instrument, at maximum current, this has been estimated at 0.25 watts which is less than one percent of the maximum thermal load for which the calorimeter was designed. Under certain conditions, for example, during the charging of a nickel cadmium cell, large currents can be associated with small or even "negative," i.e., endothermic, heat effects. These circumstances could greatly magnify the joule heat error if expressed as a percentage. Here again, it can be argued that the absolute error is still acceptably small from an engineering standpoint.

The most important objection to the Johnston type calorimeter is perhaps economic. The prototype instrument was optimized to meet a particular set of specifications, including cell size, maximum cell current, a range of cell operating temperatures, response time, and a maximum thermal load. The specified maximum uncertainty of the system was 3%.

One cannot help but ask, however, what the consequences would be if one or more of the design specifications were to be drastically changed. If an acceptable degree of accuracy could be maintained only by effecting major structural changes in the apparatus – which seems possible – then this fact alone would put the Johnston instrument in a disadvantageous position relative to the Gross design because of the cost of such a change.

Most of the above arguments are both conjectural and tentative. Calorimeters are evaluated in the laboratory, not by surmise or computation. The author is very sure of this. The data needed to make a choice are not yet available.

The need for an engineering type calorimeter is paralleled by a no less urgent requirement that an adequate scientific instrument be developed. Such a calorimeter would be a powerful new tool for the study of the processes which attend the operation of energy cells.

In this case it is not necessary that the calorimeter be able to accommodate a wide range of cell sizes since the size of the cell can be chosen to fit the size of the calorimeter rather than the reverse. It seems certain that the accuracy requirements must be much more stringent, however, even though it is impossible to state at this time just how far one must go in this direction. Experience to date with the AFTBC indicates that a maximum error of 1% under all operating conditions is a reasonable and attainable goal. The phrase, "all operating conditions" could include heat dissipation rates from 10 to 1000 mW, a temperature range of -10 to +40°C (263 to 313 K) and any current up to 6 amperes.

In view of the fact that the data in Table 1 includes errors close to 5%, such faith in the AFTBC needs substantiation. The experiments in Table 1 which fail to meet the one-percent accuracy criterion are numbers 5, 7, 9, 17, 18, 19, and 20. It is not unreasonable to disregard the 1.8% error of experiment 7 since the error decreased to 0.95% in experiment 8 after the system had been operated for a longer time and thus attained a closer approach to a steady state. Experiment 9 should be disregarded because the rate of heat dissipation, 0.7 mW, is less than the 10-mW minimum specified above and is not within the capabilities of the system.

The other experiments which have an error in excess of 1%, numbers 5, 17, 18, 19, and 20, all involved the use of a high-resistance heater for one side with a low-resistance heater on the other. The reason for a relatively large error when operating in this manner was explained in the "Discussion of Errors" section.

There are two ways to circumvent this weakness in the calorimeter. The first is to use an electrical heater on one side which is the same size and shape as the cell which is acting as a heat source on the other. Additionally, the heater and cell should both occupy the same positions in their respective calorimeter chambers. This arrangement would cause the pattern of thermal striae – and hence the heat loss – to be essentially the same on both sides, thus reducing the error from this source. If endothermic processes are to be measured, the cell itself would have to be wrapped with heater wire and the combination maintained in a null condition.

The alternative, and preferred, solution is to greatly reduce the rates of heat loss from both chambers so that significant differences in these rates on the two sides will give rise to an acceptable error. Such a reduction could be effected by using a vacuum-jacketed calorimeter chamber.

If such a major modification of the system were to be undertaken, it would be advisable to eliminate another calorimeter weakness at the same time. This weakness is a tendency of the thermopile output to become unstable if a relatively high heat dissipation rate, one watt for example, is combined with a flow rate of one cubic foot per minute or less. Under these conditions, the velocity of the downward flowing air is not great enough to overcome the tendency of the air in the vicinity of the heater to rise due to convection. The obvious solution to this problem is to reverse the direction of flow from downward to upward. This would require that the leads be brought in through an opening near the bottom of the system and then pass upward through a "chimney" into the calorimeter chamber. It would be relatively simple and advantageous to extend the vacuum jacket so that it surrounds the chimney as well as the chamber.

The behavior of the system on numerous occasions pointed to the possibility that insulating the external surface of the jacket vessel would improve accuracy. This would be neither difficult nor expensive.

The value of this report would be enhanced if it were possible to evaluate thoroughly the capabilities of the AFTBC and to compare it with other calorimeters which might compete with it as a scientific instrument. Unfortunately, the information needed to make such a comparison is not available. It is nonetheless possible to give certain generalities which might be helpful to those planning calorimetric work.

On the debit side, it has already been mentioned that the apparatus is expensive, massive, and unwieldy. In its present configuration, it is not easily adapted to large changes in cell size but with foresight and imagination, it should be possible to overcome this fault. As a final criticism, it should be pointed out that the complexity and unpredictability of some of the phenomena involved make it difficult to interpret experimental observations and thus eliminate errors by modifying the system. Reference is made, for example, to the stagnation effect dealt with previously and to heat exchangers which must equilibrate the temperature of two fluids to better than a thousandth of a degree.

Not one of these weaknesses casts a shadow on the validity or potential accuracy of the basic design.

Several inherent advantages of the AFTBC system should also be mentioned. Certainly one of these is the use of the thermal balance approach, with its automatic compensation for phenomena that would otherwise reduce accuracy. Changes in flow rate, non-linearity of the thermopile output, and heat leakage from the calorimeter chamber could be cited as examples of such phenomena.

Two other advantages derive from the use of a gas instead of a liquid as the flowing medium, and are a consequence of the thousand-fold ratio between the volume heat capacity of air as

compared with that of liquids such as oils or water. Because of this ratio, small rates of heat evolution cause relatively large and easily measured temperature changes. With the present system, for example, a signal as small as  $10 \mu\text{W}$  is easily detected. This is a very small amount of power.

The second advantage which derives from this ratio concerns what might be called base line stability or thermal noise. There is a limit to the ability of any heat exchanger to equilibrate one fluid with another, and to a first approximation it can be assumed that this limit is equally applicable to gases and liquids. It follows that for any flow type calorimeter there is practically irreducible uncertainty in the reference temperature which corresponds to an irreducible uncertainty or error in the power measurement. An advantage of the AFTBC over liquid flow calorimeters is that this power equivalent is some three orders of magnitude smaller in the case of gases than it is for liquids. In brief, the AFDC has a large signal-to-noise ratio. This is the sine qua non for any power measuring instrument if it is to be both sensitive and accurate.

## VII. ACKNOWLEDGEMENT

The author is sincerely grateful to Dr. Allan Sherman, to Mr. Thomas Cygnarowicz, and to his other friends at Goddard Space Flight Center who gave so willingly of their time, help, and encouragement, and without whom this research would have been much more difficult.

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## APPENDIX

### APPARATUS USED IN THE AIR FLOW THERMAL BALANCE CALORIMETER

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|---|--|
| (a) (Filter)<br>Ultrapore, Model MCC 100 LSU 160 VX<br>Pall Trinity Micro Corporation<br>Cortland, N.Y. 13045       | (g) (Propeller)<br>Style U, 3 blade, 10 inch diam.<br>Columbian Bronze Corporation<br>Freeport, Long Island, N.Y. 11520  |
| (b) (Air Drier)<br>Model No HA1-0000F<br>Pall Trinity Micro Corporation<br>Cortland, N.Y. 13045                     | (h) (Motor)<br>Catalogue No. VM 113-10-DS<br>Mounting B-M1<br>Boston Gear Works<br>3500 Main Street<br>Quincy, Mass. 02171   |
| (c) (Filter)<br>Part No. ACB 4463 SUOZ<br>Pall Trinity Micro Corporation<br>Cortland, N.Y. 13045                    | (i) (Null Detector)<br>Model 147<br>Keithley Instruments, Inc.<br>28775 Aurora Road<br>Cleveland, Ohio 44139   |
| (d) (Pressure Regulator)<br>Type 40-15<br>Moore Products Company<br>Spring House, Pa.                               | (j) (Potentiometer-Recorder-Controller)<br>Catalogue No. 500-632-005-0044-6-030-158<br>Leeds and Northrup Company<br>Rockland and Stenton Avenues<br>Philadelphia, Pa. 19144 |
| (e) (Pressure Regulator)<br>Type 40-7<br>Moore Products Company<br>Spring House, Pa.                                |  |
| (f) (Rotameter)<br>Type 18310, Size 3-HCF-b<br>Schutte and Koerting Company<br>Cornwells Heights,<br>Bucks Co., Pa. |  |